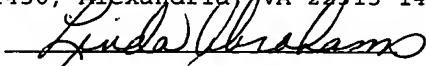


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4/12/2004

Date



Linda Abrahams

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**POWDER METALLURGY CRUCIBLE  
FOR ALUMINUM NITRIDE CRYSTAL GROWTH**

Part of the work leading to this invention was made under a United States Government STTR Contract (N00014-97-C-0362). The U.S. Government may have certain rights in  
10 this invention.

This application claims the benefit of U.S. Provisional Application Ser. No. 60/323,947, entitled Powder Metallurgy Tungsten Crucible for AlN Crystal Growth, filed September 21, 2001.

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**BACKGROUND OF THE INVENTION**

**(1) Field of the Invention**

The present invention relates generally to III-nitride semiconductors and more particularly to crucibles for growing III-nitride semiconductor substrates such as  
20 aluminum nitride (AlN). Use of the crucible of this invention may enable the growth of relatively large and high quality III-nitride single crystals.

**(2) Background Information**

Wide bandgap semiconductor devices, based on III-nitride semiconductors, are  
25 expected to find application in several opto-electronic technologies in the areas of short wavelength emission and detection. Aluminum nitride and high aluminum

concentration alloys of aluminum nitride with gallium nitride and/or with indium nitride are potentially important III-nitride semiconductors for producing deep-UV light emitting diodes with potential applications including solid-state white lighting, sterilization and disinfectant devices, compact analytical devices for the biotechnology 5 and pharmaceutical markets, bioagent detection systems, compact uv light sources for covert communication by the Department of Defense, and for short wavelength lasers for high density data storage. In addition, single-crystal substrates of aluminum nitride are attractive for the fabrication of III-nitride semiconductor, high power radio frequency, millimeter wave, and microwave devices needed for future wireless 10 communication base stations and for Department of Defense applications. However, one of the factors limiting the maturation of aluminum nitride, and other III-nitride, technology has been the absence of high-quality bulk nitride substrates.

One promising method for the growth of aluminum nitride single crystals for such substrates is the sublimation-recondensation technique first developed by Slack 15 and McNelly (“Growth of High Purity AlN Crystals”, J. Cryst. Growth **34**, 263 (1976) and “AlN Single Crystals”, J. Cryst. Growth **42**, 560 (1977)), both of which are fully incorporated by reference herein. However, one of the drawbacks that limited the maximum size of the crystals was the development of leaks in the tungsten crucibles, which ultimately lead to the failure thereof, through which aluminum gas may escape. 20 The development of crucibles that substantially eliminate this problem may provide for the growth of relatively large aluminum nitride single crystals. The need for improved crucibles for the growth of aluminum nitride single crystals has also been published, subsequent to the priority date of embodiments of the present invention, by other groups: “Properties of Crucible Materials for Bulk Growth of AlN,” G. A. Slack, J. Whitlock, K. Morgan, and L. J. Schowalter, Materials Research Society Proc. Vol. 798, p. Y10.74.1 (2004); “Crucible Selection in AlN Bulk Crystal Growth,” R. Dalmau, B. Raghothamachar, M. Dudley, R. Schlesser, and Z. Sitar, Materials Research Society Proc. Vol. 798, p. Y2.9.1 (2004); and “Sublimation Growth of Bulk AlN Crystals: Materials Compatibility and Crystal Quality,” B.M. Epelbaum, D. Hofmann, M. 25 Bickermann, A. Winnacker, Mater. Sci. Forum **389–393**, 1445 (2002).

Therefore there exists a need for an improved crucible for growth of III-nitride.

## SUMMARY OF THE INVENTION

One aspect of the present invention includes a sealable crucible for growing a III-nitride semiconductor crystal. The crucible includes a wall structure defining an interior crystal growth cavity and includes a plurality of grains. The wall structure has a thickness dimension extending in a direction substantially perpendicular to the longitudinal direction, the thickness dimension being at least about 1.5 times the average grain size.

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In another aspect, this invention includes a sealable crucible for growing a III-nitride semiconductor crystal. The crucible includes an elongated wall structure extending in a longitudinal direction. The wall structure defines an interior crystal growth cavity and includes a plurality of grains. The grains effectively form at least first and second layers, the first layer including grains disposed on an inside surface of the crucible and the second layer being adjacent to the first layer.

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In still another aspect, this invention includes a method for fabricating a crucible for use in growing aluminum nitride single crystals. The method includes providing a bar of powder metallurgy material and machining an elongated wall structure extending in a longitudinal direction. The wall structure defines an interior crystal growth cavity and includes a plurality of grains. The grains effectively form at least first and second layers, the first layer including grains disposed on an inside surface of the crucible and

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the second layer being adjacent to the first layer.

In yet another aspect, this invention includes a method for fabricating an aluminum nitride single crystal. The method includes providing a crucible having an elongated wall structure extending in a longitudinal direction; the wall structure defining an interior crystal growth cavity and including a plurality of grains, which effectively form at least first and second layers, the first layer including grains disposed on an inside surface of the crucible and the second layer being adjacent the first layer. The method further includes charging the crucible with aluminum nitride, sealing the crucible, and heating at least a portion of the crucible to a temperature in excess of about 2000 degrees C.

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## BRIEF DESCRIPTION OF THE DRAWINGS

**Figure 1** is a cross-sectional schematic representation of a prior-art thin wall crucible;

5      **Figure 2A** is a cross-sectional schematic representation of a portion of the crucible of Fig. 1 prior to grain growth;

**Figure 2B** is a cross-sectional schematic representation of the portion of the crucible shown in Fig. 2A after exposure to Al vapor at growth temperatures;

**Figure 3A** is a view similar to that of Fig. 2A, of a portion of a crucible of this invention prior to grain growth; and

10     **Figure 3B** is a cross sectional schematic representation of the portion of the crucible shown in Fig. 3A after exposure to Al vapor at growth temperatures.

## DETAILED DESCRIPTION

Referring briefly to Figs. 3A and 3B, the present invention includes a crucible 15 that may be useful in growing relatively large aluminum nitride and/or other III-nitride single crystals for use in semiconductor applications. A tungsten crucible is described in this particular example. This is for illustrative purposes only and those skilled in the art will recognize the detailed description provided herein could be applied in a straightforward fashion to various other crucible materials such as described with 20 respect to alternate embodiments described herein. The tungsten crucible 100 of this invention includes a wall structure having a thickness 126 that is at least about 1.5 times, and preferably greater than about 3 times, that of the average tungsten grain 122. In one embodiment, the tungsten crucible 100 is formed using powder metallurgy techniques.

The crucible of the present invention may advantageously provide for the growth 25 of relatively large III-nitride single crystals, and in particular may provide for the growth of AlN single crystals having a diameter in the range from about 20 to about 50 mm or greater. AlN crystals of this size may be advantageously used to fabricate relatively high quality nitride semiconductor devices with relatively better yield than prior-art approaches. These and other advantages of this invention will become evident 30 in light of the following discussion of various embodiments thereof.

Referring now to Figs. 1-3B, prior art and the apparatus and method of the present invention are described. Referring to Fig. 1, prior-art crucible 10 typically includes a cylindrical body portion 12 and a tapered conical end portion 14 and is used

in a tungsten tube furnace such as that shown in the above-referenced Slack and McNelly ("AlN Single Crystals"). To grow AlN crystals using the sublimation-recondensation technique of Slack and McNelly, the sharp tip 16 of the crucible is placed in the nominal center of the furnace at the start of run with a charge of AlN (e.g., 5 about 5 grams) placed at the opposite end 18 of the crucible 10. The crucible 10 is rotated (e.g., at about 2 revolutions per hour) about its longitudinal axis 15 and simultaneously pushed through the hot zone (i.e., the center) of the tube furnace (with end 18 moving towards tip 16) at a rate of about 0.3mm per hour. The center of the furnace is held at a temperature of about 2250 degrees C during the duration of the run.

10 The total running time may be on the order of 100 hours or more.

Referring now to Fig. 2A, these conventional crucibles 10 are formed by a chemical vapor deposition process (CVD). Crucibles 10 formed by a CVD process (e.g., using either the conventional tungsten fluoride or tungsten chloride processes) may be characterized as having a columnar grain structure in which the W grains 22 are 15 disposed substantially perpendicular to the inner wall 24 of the crucible 10 and extend substantially the entire thickness 26 of the crucible wall 20 (i.e., from the inner wall 24 to the outer wall 25). Referring now to Fig. 2B, and as briefly described hereinabove, crucible 10 tends to develop pinhole leaks 30 at the grain boundaries 32 (Fig. 2A) thereof, which disadvantageously permit aluminum vapor to escape from the interior of 20 the crucible 10. The pinhole leaks 30 also generally lead to crucible failure which thus limits the maximum achievable crystal size.

This problem may be circumvented, in theory, by employing single-crystal tungsten crucibles. However, such a solution is relatively difficult to implement and prohibitively expensive for commercialization.

25 One aspect of this invention is the realization that the above-described pinhole leak problem may be related to swelling of the tungsten grains 22 caused by the absorption of aluminum during use. Measurements conducted by the inventors have shown that after growth at 2330 degrees C the tungsten crucible contained 5.3 atom percent aluminum in solid solution (which is approximately equivalent to the saturation 30 value of aluminum in tungsten at that temperature). At this aluminum concentration, the lattice constant was measured to decrease slightly to 3.162 angstroms from 3.165 angstroms for pure tungsten (with aluminum atoms substitutionally replacing tungsten atoms in the lattice). Thus the absorption of aluminum should theoretically result in

swelling of slightly less than 5.3 volume percent, which was corroborated by an observed swelling of about 5 volume percent.

Not wishing to be bound by a particular theory, it is believed that the swelling results in pinhole 30 formation, particularly at the triple points where three tungsten grains 22 meet. Since the grains 22 of the CVD tungsten crucibles 10 are columnar and extend the thickness 26 of the crucible wall 20, the pinholes 30 likewise extend the thickness 26 of the crucible wall 20.

Referring now to Figs. 3A and 3B, a cross sectional schematic illustration of the tungsten grain 122 structure of the crucible 100 of the present invention is illustrated. Crucible 100 is substantially similar to crucible 10 (Fig. 1) in that it may include a cylindrical body portion 12 (Fig. 1) and a tapered conical end portion 14 (Fig. 1). Crucible 100 differs from that of crucible 10 in that it utilizes a granular, multigrain structure in which the thickness 126 of the crucible wall is at least 1.5 times that of the average grain diameter. The grain structure of this invention may also be thought of as including at least two layers, a first layer 144 adjacent to (or forming) the inner wall 124 of the crucible 100 and a second layer 145 adjacent to the first layer 144. While not wishing to be bound by a particular theory it is believed that the present invention uses the normally deleterious effects of the grain swelling to advantage, to nominally block grain boundary diffusion. It is believed that once swelling has occurred along grain boundaries 132 of the first grain layer 144, further diffusion is severely hampered by the second grain layer 145, grains of which have swollen to effectively close off any diffusion pathways or pinholes along the grain boundaries of the first layer 144. Thus, any further diffusion of aluminum into the walls of the crucible generally occurs only by relatively slow bulk diffusion. Further, the three-dimensional, substantially random arrangement of the grains 122, as illustrated in Figs. 3A and 3B, is believed to slow the formation of pinholes in any of the layers. Nevertheless, aluminum transport through any pinholes that may be formed in the first layer 144 of tungsten grains 122 is nominally sealed off by the second layer 145 (or subsequent layers) thereof.

One method of implementing this invention is to machine crucibles from a tungsten bar formed using powder metallurgy techniques. These powder metallurgy bars include tungsten grains having substantially no columnar grain structure. As stated above, this structure is believed to reduce the penetration rate of aluminum along the grain boundaries and its subsequent escape from the crucible, particularly after the

tungsten grains have swelled due to the uptake of Al by bulk in-diffusion. Crucibles formed by the above described powder metallurgy technique have been demonstrated to exhibit a significantly longer life than would be expected simply by the increased wall thickness, indicating that the granular structure slows the permeation of aluminum  
5 through the crucible walls.

The artisan of ordinary skill in the art will readily recognize that there may be alternate approaches to forming a multilayered tungsten crucible wall. One such possible approach may be to fabricate crucibles using multiple CVD steps while using an agent between steps that disrupts further columnar growth of the individual tungsten  
10 grains.

The crucible of the present invention may be useful in fabricating III-nitride single crystals such as aluminum nitride for the electronics and opto-electronics applications. For example, the inventive crucible may be used in a tube furnace, such as that disclosed by Slack and McNelly as referenced hereinabove. The crucible is  
15 typically first charged with relatively pure aluminum nitride (e.g., greater than about 99%) and then sealed before inserting into the tube furnace. At least a portion of the crucible is heated to a temperature in excess of about 2000 degrees C at which aluminum nitride crystal formation is favored.

The crucibles of the present invention have been demonstrated to successfully  
20 grow AlN crystals having a diameter of up to 20 mm and greater. Moreover, the powder metallurgy tungsten crucibles of this invention may be used to grow AlN crystals having a diameter of up to 50 mm or greater. As described hereinabove, AlN crystals of this size may be advantageously used in the fabrication of relatively high quality nitride semiconductor devices with relatively better yield than prior approaches.  
25

Specific exemplary embodiment(s) have been disclosed herein in which a multilayered and/or three-dimensional nominally random tungsten grain structure is produced resulting in the boundaries between tungsten grains being nominally completely blocked owing to the swelling generated by aluminum absorption. In light thereof, the skilled artisan will readily recognize that any approach to tungsten crucible  
30 construction that creates multiple layers of relatively dense tungsten grains, may be considered within the spirit and scope of this invention.

Other embodiments are also envisaged in which tungsten crucibles are subjected to a sealing process through grain swelling with metals other than aluminum. For

example, Be, Cr, Pd, Ti, Pt, Rh, Ru, and V each have high temperature solubilities in tungsten (*S.V. Nagender Naidu and P. Rama Rao, Editors, Phase Diagrams of Binary Tungsten Alloys, Indian Institute of Metals, Calcutta, (1991)*). Thus they would be expected to swell the tungsten grains and nominally stop further grain boundary diffusion of the chosen metal or, on later reheating, of Al in the crucible of this invention. Metals with somewhat lower solid solubility in tungsten (such as Fe) may also be effectively contained by grain swelling although the solid solubility of Fe in tungsten is less than three percent. It may also be possible to fabricate crucibles out of metals other than tungsten in which the solid solubility of the metal contained by the crucible causes the grains of the crucible to swell and thus impede further grain boundary diffusion of the metal contained therein.

One disadvantage of tungsten crucibles is that pure tungsten tends to be quite brittle and, as a result, is difficult to machine. Accordingly, alternate embodiments of the present invention may be provided, which are substantially similar to crucible 100 described hereinabove, though fabricated from various materials other than tungsten.

For example, in particular embodiments, crucibles may be fabricated from tungsten-rhenium (W-Re) alloys, which tend to be much less brittle thus useful in situations where some machinability or flexibility is desired. Pure tungsten has a body-centered-cubic crystal structure and W-Re alloys will have nominally the same crystal structure up to 37 atom% rhenium. Aluminum atoms diffused into such W-Re alloy grains will produce the desired grain swelling and reduced grain boundary diffusion as described above. Thus, such W-Re polycrystalline alloy crucibles may be employed for growing AlN crystals. Since the W-Re mixed crystal grains have a melting point lower than that of pure tungsten, these crucibles may be limited to AlN crystal growth temperatures lower than those used for pure W. If the upper use temperature in a particular implementation is, for example, about 2350 °C for a pure tungsten crucible, then one would expect the upper growth temperature to be limited to about 2000 °C for a crucible fabricated from tungsten containing 37 atom% rhenium in an otherwise similar implementation.

Other embodiments may include crucibles fabricated from polycrystalline rhenium (Re), which has a hexagonal-close-packed crystal structure. Aluminum atoms are also substitutionally soluble in rhenium at high temperature, and may be used to eliminate porosity in polycrystalline rhenium by using a multilayer grain structure. The

first (e.g., inner) layer of Re grains will also swell as described above, sealing off the later (e.g., outer) layers of grains.

Still further embodiments include crucibles fabricated from polycrystalline tantalum monocarbide, (TaC). These crucibles would also be chemically stable in the presence of AlN and in a nitrogen atmosphere of up to 100 bars at 2300 °C. Thus, crucibles of TaC may be useful for growing AlN. However, polycrystalline crucibles of TaC would generally be slightly porous and Al vapor will leak out of them during growth unless a multilayer grain structure is used such as described hereinabove. One way the present invention may be applied to these crucibles is by fabricating them using a powder mixture of TaC with added Ta<sub>2</sub>C. For instance, a pressed and sintered crucible, using powder metallurgy, may be made from about 10 volume percent of Ta<sub>2</sub>C added to the TaC. When the sintered crucible is fired in CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, or other suitable hydrocarbon gas at 2000 °C to 2500 °C, the Ta<sub>2</sub>C will convert to TaC and will increase its volume by about 7.5% so that it would eliminate about 0.75 volume percent of porosity in the finished crucible. Employing a 50 volume percent TaC plus 50 volume percent Ta<sub>2</sub>C would enable one to fully eliminate about 3.8% volume percent porosity in the sintered body.

In a variation of these embodiments, tantalum (Ta) metal powder may be added to the TaC powder mixture at the start of the powder metallurgy process. This Ta metal will expand by about 23% in volume when converted to TaC. Thus, less second-phase material is required to make a dense TaC crucible body. Such dense, multi-grain crucibles may be very useful for growing AlN crystals as described herein.

Still further embodiments include crucibles of polycrystalline Ta<sub>2</sub>N, which may be used for growing AlN crystals at temperatures up to about 2300 °C (depending on the Ta<sub>2</sub>N/AlN eutectic temperature). Useful crucibles may be formed by using powder metallurgy starting with a mixture of Ta<sub>2</sub>N powder and Ta metal powder. In particular examples, after pressing and sintering, these crucibles should be heated in about 0.1 to 10 bars of N<sub>2</sub> gas at 2000 °C before use. During this heat treatment, the Ta powder grains will be converted to Ta<sub>2</sub>N and will expand by about 9.5% in volume. Thus, residual porosity in such crucibles may be nominally eliminated before being used to grow AlN crystals. Moreover, use of multilayer grain structures, such as described

hereinabove, will dramatically reduce Al diffusion along the grain boundaries through the crucible walls allowing large AlN crystals to be grown.

In other embodiments, crucibles of polycrystalline hafnium nitride (HfN) may also be used for growing AlN crystals up to temperatures of about 2300 °C. These 5 powder metallurgy crucibles may be made from a mixture of HfN powder and hafnium (Hf) metal powder. If such crucibles are heated in 0.1 to 10 bars of N<sub>2</sub> gas at 2000 °C before use, the Hf powder grains will be converted to HfN and will expand by approximately 7.3% in volume during the process. Thus, residual porosity in such crucibles may be nominally eliminated before use for growing AlN crystals. And, as 10 discussed above with respect to other embodiments, these crucibles may be fabricated with multilayer grain structures, to retard Al diffusion along the grain boundaries through the crucible walls allowing large AlN crystals to be grown.

Other embodiments include powder metallurgy crucibles fabricated from a mixture of W and Ta powders. These two metals are mutually miscible in all 15 proportions to form homogeneous alloys. Thus, a crucible made from an alloy of, for example, 3 atom percent Ta, may be formed. A range of Ta contents from 0.5 to 10 atom percent are also possible. When such a polycrystalline crucible is heated in N<sub>2</sub> gas at 2000 °C at 0.1 to 10 bars pressure, the nitrogen atoms will diffuse into the alloy grains. There will be no chemical reaction with the W but the Ta metal will react with 20 nitrogen to form Ta<sub>2</sub>N clusters. These Ta<sub>2</sub>N clusters have a hexagonal-close packed crystal structure and will precipitate out at the grain boundaries in the body-centered-cubic W. Thus, they will act as grain-growth inhibitors keeping the grain size of the W grains relatively small. This small-grain-structure is useful when the crucibles are exposed to Al vapor in the growth of AlN crystals. Such small grains rapidly become 25 saturated with aluminum and thus expand to stop the grain-boundary transport of aluminum, e.g., when in a multilayer construction as discussed hereinabove. Such W-Ta crucibles should self-seal more rapidly than pure W crucibles, and thus be better for growing AlN crystals.

The modifications to the various aspects of the present invention described 30 hereinabove are merely exemplary. It is understood that other modifications to the illustrative embodiments will readily occur to persons with ordinary skill in the art. All

such modifications and variations are deemed to be within the scope and spirit of the present invention as defined by the accompanying claims.